"Synthesis, Spectroscopic, Kinetic And Biological Studies Of Copper (II) Neem And Copper (II) Pongamia Soaps And Their Complexes"

Submitted to

MAHARSHI DAYANAND SARSWATI UNIVERSITY, AJMER

For

Ph. D (Chemistry)

By

Priyanka Kumawat

Under The Supervision & Guidance Of

Dr. Rashmi Sharma
Associate Professor
SPC Govt. College, Ajmer (Raj.

Format of Synopsis
M.D.S. University, Ajmer

1. Name of Scholar (In English) :- PRIYANKA KUMAWAT
   (In Hindi) :- प्रियंका कुमावत
2. Title of the Research Work :
   (In English) :-SYNTHESIS, SPECTROSCOPIC, KINETIC AND BIOLOGICAL STUDIES OF COPPER (II) NEEM AND COPPER (II) PONGAMIA SOAPS AND THEIR COMPLEXES
   (In Hindi) :- ताम्र (II) नीम व ताम्र (II) करंज साबुन एवं उनके संकुलों का संश्लेषण, स्पेक्ट्रोमितीय, गतिकीय और जैविकीय अध्ययन
3. Location
   a. Institution/Department where the work is to be done :- Samrat Prithviraj Chauhan Government College,Ajmer

   b. Geographical area of Investigation if any :- 1. Samrat Prithviraj Chauhan Government College,Ajmer
      2. Maharshi Dayanand Saraswati University, Ajmer
      3. Central Arid Zone Research Institute, Jodhpur (Rajasthan)-342005
      4. Medical College , Jodhpur (Rajasthan)-342005

- Introduction Importance of Proposed Investigation, Objectives.:- [Enclosure-1]
- Review (Work already done on the subject of proposed Research Study):- [Enclosure-2]
- Research Gaps identified in the proposed field of investigation. (Based on the review) :- [Enclosure-3]
- Major Hypothesis, if any. :- [Enclosure-4]
- Research methodology. :- [Enclosure-5]
- List of references cited. :- [Enclosure-6]

प्रियंका कुमावत 13.05.2016

Signature of the Candidate with date
(Priyanka kumawat)

13-5-16.

Name and Signature of supervisor with date & seal.
(Dr. Rashmi Sharma)

Samrat Prithviraj Chauhan
Govt. College, Ajmer

Enclosure -1

Introduction Importance of proposed investigation, objective –

Photo catalysis has been considered as a part of green chemistry, therefore photochemical degradation of any substance will be an eco-hyphen approach. It is also considered as an advance oxidation process (AOP). [1-3]

Copper has efficiency to bind with fatty acids and oils to form copper soaps. Copper (II) soaps in polar and non polar solvents are used in emulsification, wetting, lubricating and foaming due to their surface active properties. [4]

Combination of copper soaps with heterocyclic ligands play wonderful role in various fields. They show fungicidal, pesticidal, insecticidal and nematocidal activities. [5-6]

Various semiconductors are used as photo catalysts for photo degradation of different organic pollutants in industrial effluents and / or waste water. Copper complexes have a wide diversity of uses in the electrical refrigeration and heavy industries in powder metallurgy and in communications. [7-10]

Copper soaps have a tendency of complexation with 'nitrogen' and 'sulphur' containing ligands mixed ligand complexes of copper play important role in numerous chemical and biological system like water softening, electroplating, dyeing, antioxidant, photo-synthesis in plants removal of undesirable and harmful metals from living organisms etc. [11]

Copper complexes have many applications in various fields like wood preservative dyeing, detergency, electroplating, foaming, wetting, herbicidal, pesticidal activities, paints, lubrication, emulsification etc. [13]

Various oils and fats are of great biochemical importance because of their role as chief storage form of energy, which serves as building stone. In addition to edible purpose they are also commercially important in the form of medicine, soaps, detergents, lubricants, greases and in various paints and varnish industries. [14-16]

Numerous methods have been developed for measuring free fatty acids in milk to estimate the intensity of lipolyzed flavor. The most frequently used method in this country is the Bureau of Dairy Industry (BDI) method developed in 1955 by Thomas et., al. [17]

Copper ions, either alone or in copper complexes, have been used for centuries to disinfect liquid solids, and human tissue. Today copper is used as a water purifier, algaecide, fungicide, nematocide, molluscicide, and antibacterial and antifouling agent. Copper also displays potent antiviral activity. We hypothesized that introducing copper into clothing, bedding, and other articles would provide them with biocidal properties. A durable platform technology has been developed that introduces copper into cotton fibers, latex and other polymeric materials. [18-21]

Objectives

Various edible oils like sesame, coconut and non edible oils like neem, pongamia are widely used for medicinal purpose the copper (II) soaps in polar and non polar solvents having remarkable interest and find their uses in various fields of applications like foaming, wetting, emulsification etc due to the surface active properties of soaps.

The main objectives of the proposed research work are as follows:-

1. Synthesis of copper soaps.
2. Purification of copper soaps.
3. Synthesis of complexes.
4. Purification of complexes.
5. Spectroscopic studies IR, NMR, ESR, etc of soaps and complexes.
6. Photo degradation to study the effects of different factors likes concentration of soap, PH, semiconductor etc of soaps and complexes.
7. Thermo-gravimetric analysis (TGA) studies of soaps and complexes.
8. Biological studies of copper soaps and complexes.

Enclosure -2

Review (work already done on the subject of proposed research study)

The research work possesses an important role in the current scientific development, plenty of work is going on in various laboratories and industries at national and international level. The physical, analytical and spectral investigations of various oils have been already done.

The semi solid copper (II) soaps derived from some oils like ground nut oil and sesame oil have been synthesized and characterized by elemental analysis IR and NMR spectroscopy. The spectroscopic data like IR, NMR, ESR and Thermo-gravimetric analysis (TGA) investigation of these soaps and their complexes are of great importance. [22-23]

Some non edible oils are antibacterial, antiviral, antifungal, antiseptic and anti-parasitic like neem oil. Neem oil is also excellent insect repellant, pongamia oil is suitable as row material for biodiesel fuel. [24]

Some oils like neem and mustard used as potential biotical agents and wood preservatives and analysis of their thermo-gravimetric and other properties will generate a new hope in biological and pharmacological fields. [24-25]

Copper soaps derived from edible oil i.e. mustard and soya-bean play a vital role in various fields due to their surface active properties. Some edible oils like mustard, soya-bean, sesame oil etc are high in antioxidant that protect against sun and air pollution. [11-12]

The U.V. photolytic degradation of butyl tin chloride in water gas has been investigated. [26] Photo oxidation of acetic acid by oxygen in presence of titanium dioxide and dissolved copper ions have been investigated. [27]

Copper shows poisonous effect when its concentration up to 44 mg/L especially if the water has a high PH value (around 7.0). Effect of PH and concentration on reactivity of copper has been studies earlier. [28-29]

Copper fungicide sprays are always more effective at controlling and preventing diseases if applied before a plant become overrun with said disease.

Copper soaps and non polar solvents have gained a considerable interest and find their uses in various fields of application because of their properties as surfactants, dyes and organic pollutants. [30-33]

Copper complexes with edible oils have many applications in various fields like foaming, wetting, herbicidal, pesticidal, fungicidal, detergency, emulsification, paints, woods, lubrication etc. [8-9]

Fungicides and pesticides that specifically inhibit or kill fungi underlying diseases important to man. Understanding mechanisms of fungicide action and toxicity is important because humans and domesticated animals encounter these pesticides through a wide variety of applications. In agriculture, fungicides are used to protect tubers, fruits and vegetables during storage or are applied directly to ornamental plants, trees, field crops, cereals and turf grasses. [34-35]

In veterinary medicine, fungicides are commonly an antibacterial/antiseptic treatment for foot rot disease but, some fungicides (e.g., copper sulphate), are also used amolluscicide to repel and kill slugs and snails. Another example of dual use of fungicides is the treatment by the widely used agricultural fungicide benzothiazole against intestinal parasites in both human and veterinary medicine. [36-37]

Copper sulphate is also known as bluestone, blue vitriol, blue copperas. The chemical name is cupric sulphate pentahydrate . It is used to control bacterial and fungal disease of fruit, vegetable, nut and field crops. Some of the disease that is controlled by this fungicide includes mildew, life spots, blights and apple scab. [38-39]

Triazole fungicides, which exhibit their antifungal activity by inhibiting fungal ergosterol biosynthesis, are economically important agricultural chemicals as they are widely used on crops such as wheat, barley, and orchard fruits. However, in spite of their widespread use, toxicity evaluations have been performed only within regulatory submission requirements for many of the triazole fungicides. Comprehensive data assessing their biological effects has been very limited, and in the case of certain triazole fungicides (e.g., tebuconazole), almost completely lacking. Moreover, data addressing possible adverse effects of triazole fungicide exposure during development is even more limited. [40-41,68]

Enclosure -3

Research gaps identified in the proposed fields on investigation (based on the review)

Reference on the related subject reveals the importance of the proposed field. For this purpose literature survey from different universities and searching through internet had been done. It has been found that plenty of work need to be done in the proposed field.

Photo catalytic degradation has been considered to be an efficient and rapid process for the degradation of copper soaps derived from edible and non edible oils. [42]

The photo catalytic degradation of some copper soaps may be studied spectro photo metrically in non aqueous and non polar solvent benzene using zinc oxide or titanium-di-oxide as semiconductor. Further some other oils and semiconductors may taken for studies. [43-44]

Thermo-gravimetric analysis (TGA) is a thermal analysis technique which measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. [45]

TGA measurements may be used primarily to determine the composition of soaps and to predict their thermal stability up to elevated temperatures. The use of thermo-gravimetric data to evaluate kinetic parameters of solid-state reactions involving weight loss (or gain) has been investigated by a large number of workers. [46-47]

Some of the fungicidal, bactericidal studies may also be done as the sulphur and copper based products can be used for growing organic products. Literature survey reveals that some fungicides work better (study on the plant longer or spread over the leaf surface) if a spreader sticker is mixed with the solution.

Enclosure -4

Major Hypothesis, if any

The copper (II) soaps in polar and non polar solvents having remarkable interest and find their uses in various fields of applications like foaming, wetting, emulsification and lubrication etc due to the surface active properties of soap. [48-50]

Copper soap complexes of colloidal behavior play a significant role in various fields like preservatives herbicidal, pesticidal activities, detergency, paints, lubrication etc. [51-52]

In biological systems, these agents are vital components and useful in many industrial process like stabilizers, printing, fabrics, photo- sensitizers and indicators. All these properties led us to study physicochemical and biological parameters of various copper soap complexes. [12,53-54]

Therefore the proposed research work will generate new aspects in biological and pharmacological fields due to the biological importance of synthesized compounds and their application stimulated our interest to extend.

The facts mentioned above lead to a curiosity about what results shall be obtained when copper complexes undergoes photo catalytic degradation and how to effects by factors likes PH, semiconductors, concentration of soap, amount of semiconductor, effect of light intensity etc on the rate of degradation process. [55-56]

Thermo-gravimetry has been employed to study the kinetics of thermal decomposition of Copper-neem soap and Copper-pongamia soap. Thermo-gravimetric Analysis method for kinetic analysis is reported here. This technique which measures the weight change in a soap as a function of temperature and time, in a controlled environment. [57]

Fungicides are often used in combinations with other pesticides and carriers or solvents which, in combination, may be more toxic than estimated for any one of the compounds. [39]

Enclosure-5

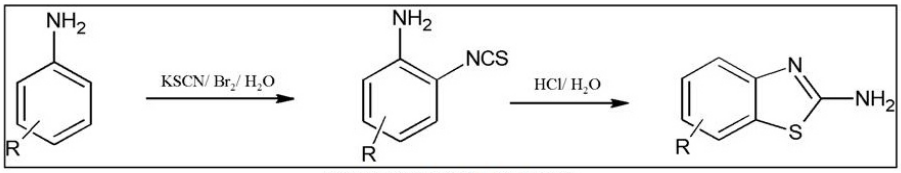
Research Methodology

Synthesis

(A) Synthesis of Metal Soaps :- Copper soaps will be prepared by refluxing the non edible oils (i.e. neem oil, karnja oil, castor oil and nicotiana tabacum oil) extracted from kernels and purified. Copper surfactants are prepared by direct metathesis of the corresponding potassium soap with slight excess of required amount of copper sulphate at 65-70^{0}c. After washing with hot water and alcohol the sample will be dried and recrystallized with hot benzene. [58-60,65]

$$RCOOH \xrightarrow{KOH\ /EtOH} RCOOK \xrightarrow{Cu+2} (RCOO)_2Cu$$

(B) Synthesis of Substituted Benzothiazole :- It will be synthesized by thiocyanogenation of substituted aniline in the presence of thiocyanogen gas, which will generated in situ by the reaction of cupric chloride and ammonium thio-cyanate. After cooling sodium carbonate will be mixed to neutralize the mixture and to get the substituted benzothiazole. [60-63]



SYNTHESIS USING ANILINES

(C) Synthesis of complexes :- The complexes will be prepared by mixing the metal surfactants and ligands (Urea /Thiourea /Benzothaizole /Nitrogen and Sulphur donor) in the molar ratio 1:2 dissolving in ethanol and mixture is refluxed for *about* 1-2 h. The formation of complex will be confirmed by using IR, NMR techniques and elemental analysis. The purity of the complex will be confirmed by TLC. [62]

2. Spectroscopy studies of copper soap and complex :- The semi solid copper soaps derived from non edible oils likes neem oil and karnja oil will be synthesized and characterized by elemental analysis IR, ESR and NMR spectroscopic spectral studies.[23-24]

3. Photo-catalytic degradation studies of copper soap and complex :- Photo-catalytic degradation has been considered to be an efficient and rapid process for the degradation of copper soaps derived from edible and non edible oils.[44,55]
4. Thermo-gravimetric analysis of soap and complex :- The copper soaps derived from these oils will be thermally analyzed using TGA technique to determine their energy of activation. [48,64]
5. Biological studies of copper soap and complex :- Concern copper soap fungicide is another organic copper based product that will protect and control any disease. The antibacterial activities of copper soap and their complexes will be evaluated by testing against available bacteria, which will be isolate and then purify and identify. [63,66-67]

Enclosure -6

List of References :-

1. Pal A. and Dass G., *J. Indian Chem. Soc.,* 76, 446-451, 1999.
2. Maheshwari G. and singh M., *J. Indian Chem. Soc.,* 79, 659-664, 2002.
3. Jagegoud Y. Ijare O.B., Mallikarjuna S.D. and Mruthyunjayaswamy B.H.M., *J. Indian Chem. Soc.,* 79, 921-924, 2002.
4. Mathur, N. *J. Chem. Pharm. Sci.,* 1(1), 37-51, 2011.
5. Jevtovic, V., Ivkovic, S., Kaisarevic, S. and Kovacevic, R. *Contemporary Materials,* 1(2) 133-137, 2010.
6. Srivastava, K., Srivastava, K.A. and Jagdish, P. *J. Indian Chem. Soc.,* 8, 661-664, 2012.
7. Michell A.J., *Holzforschung,* 49, 3, 217-221, 1995.
8. Conradie D., Turner P., Conradie W.E., pendlebury J. and Pizzi T*., Bibliographic Citation, Div. of forest science and technology. Stochholm (Sweden),* 22, 1995.
9. Mehrotra K.N. and Pooranchand, *Tenside Surf. Det.,* 25(3), 180-185, 1988.
10. Mehrotra K.N. and Pooranchand, *Tenside Surf. Det.,* 27(6), 393-395, 1990.
11. R. Sharma and S. Khan, *RPMP Natural Products,* 18, 429, 2007.
12. M. R. K. Sherwani, R. Sharma, A. Gangwal and R. Bhutra, *Indian J. Chem.,* 42A, 2527, 2003.
13. Swami M.B. and Akuskar S.K., *Int. J. Chem. Sci.,* 6(1), 87-93, 2008.
14. Sparks C.S. (Cuprinol Ltd. Engl.) Rec. Annu*, Conv.Br. wood Preserv. Assoc*., 48-51, 1978.
15. Hussain S., Shahid H. and Asjad S., Pakisthan, *J. Sci. In. Res.,* 10(3), 197-200, 1967.
16. Mahapatra B.B. and Mishra R.R*., J. Indian Chem. Soc.,* 78, 395, 2001.
17. Thomas, E. L., A. J. Nielson, and J. C. Olson*, Am. Milk Rev.* 77(1), 50, 1955.
18. Dollwet, H. H. A., and Sorenson, J. R. J. Historic, *Trace Elem. Med.* 80–87, 2001.
19. Weber, D. J., and Rutala, W. H. (Williams and Wilkins, New York) , 415–430, 2001.
20. Fraser, W. D., Quinlan, A., Reid, J., Smith, R. N., *INCRA Project no.* 211, *Huntingdon Research Center*, 43, 2001.
21. Tal, M. Metallized *textile. MTC Ltd. (U.S. patenet 5*,871,816). February 16, 1999
22. Sharma R, Tank P, Saxena M, Bhutra R and Ojha KG. *Tenside Surf Det* 45(2), 87-92, 2008.
23. Sharma R and Khan S. *Tenside Surf Det* 46(3), 145-151, 2009.
24. Sharma S.M. *"Vegetable Oils",* ISBN; 81-86, 321-55-1, 2003.
25. Bhandari S., Vardia J., Malkani R.K. and Ameta S. C., *"Toxilogical and Environmental Chemistry",* 88(1), 35-44, 2006.
26. Navio J.A., Marchena F.L., Cerrillos C. and Pablos F., *J. Photochem. Photobiol.,* 71A, 97, 1993.
27. Bidueau M., Claudel B., Faure L. and Kazouan H*., J. Photochem. Photobiol*, 61A, 269, 1991.

28. Grushko Y.M., Vrednye Neoganichesbie Soyedineniya Promyshlennykh. Stochnykh Vodakh. *"Harmful Inorganic Compounds in Industrial Waste Water".* Khimiya, Liningrad (In Russian), 1979.
29. Nagaraj G., *"Oleochemicals from vegetable oils and fats-an overview".* In Nagaraj G.estal. (eds), oil seed quality and value added products. Directorate of oil seeds Research, Hyderabaad, 37-41, 1995.
30. Ameta S.C., Punjabi, P.B., Rao P. and Singhal B, *J. Indian Chem. Soc.,* 77, 157, 2000.
31. Sighal B., Dangi G., Vardian J. and Ameta S.C*., Poll Res*., 19(2), 219, 2000.
32. Ameta R., Vardia J., Punjabi P.B. and Ameta S.C*., Indian J. Of Chem. Tech.,* 13, 2006.
33. Vaya D., Benzamin S., Sharma V.K. and Ameta, S.C*., Bulletin of catalysis Society of India,* 7, 56-66, 2008.
34. Gupta, P.K. & Aggarwal, M. Toxicity of fungicides. In: *Veterinary Toxicology*, Gupta, R. C. (Ed.), 1st ed Elsevier*,* 978-0-12-370467-2, New York., 587- 601, 2007.
35. Hartley, D. & Kidd, H. (Eds.) *The Agrochemicals Handbook*. *Royal Society of Chemistry,* 0851864066, Nottingham., 1983.
36. Ortolani, E.L.; Antonelli, A.C. & Sarkis, J.E.S. Acute sheep poisoning from a copper sulphate footbath. *Veterinary and Human Toxicology,* 46, 6, 315-318, 0145-6296., 2004.
37. Lorgue, G.; Lechenet, J. & Rivière, A. *Clinical Veterinary Toxicology,* Blackwell Science, 0-632-03269-3, London., 5-194, 1996.
38. Osweiler, G.D.; Carlson, T.L.; Buck, W.B. & Von Gelder, G.A. (Eds). Organic Synthetic Fungicides. In: *Clinical and Diagnostic Veterinary Toxicology*, 3rd ed., Kendal/Hunt, 0-8403-3332-3, Dubuque., 231-242, 1985.
39. U.S. Environmental Protection Agency,Pesticide Programs, U.S. Government Printing Office, Washington, DC. *Fact sheet no 100*., 1986.
40. Buchenauer, H. *Mechanism of action of triazolyl fungicides and related compounds,* (H. Lyr, Ed.), Wiley, New York. pp. 205–231, 1987.
41. Machera, K. Developmental toxicity of cyproconazole, an inhibitor of fungal ergosterol biosynthesis, in the rat. *Bull. Environ. Contam. Toxicol.* 54**,** 363–369, 1994.
42. Ameta S.C*., J. Indian Chem. Soc.,* 79, 305-307, 2002.
43. Nefedov V.N., Kuzmina E.A., Martynov I. Yu., Mashtalir N.N., Kisilitra P.P., Barachevskii V.A., Ir. Vses. Kihifotointa, 69, 1985.
44. Pelizzetti E., Minero C., Pramauro E., Barbini M., Maurino V., Tosata M., *Chem. Industr.,* 69, 88, 1987.
45. Gopalkrishnan S and Sujatha R. Pelagia Research Library, *Der Chemicia Sinica* 2(5), 103-117, 2011.
46. Yu, Dawei and Utigard, Torstein A. *Thermochemicia Acta* 533, 56-65, 2012.
47. Jrlic, Dijana, Tomic-Tucakovic, Biljana and Mentus, Salvko. *Thermochemicia Acta* 521, 211-217, 2011.
48. J. Hostynek and H. Maibach, *Toxicol. Mechan. Methods*, 16, 245, 2006.
49. K.K. Czeslaw, *Tribology Internat.*, 38, 337, 2005.
50. R.N. Patel, S. Kumar and K.B. Pandeya, *Indian J. Chem.*, 39A, 1124, 2000.

51. J.L. Soyez, Brighton Crop*, Protection Conference, Pest and Diseases, France,* Vol. 1, pp. 451-456, 1992.
52. S.N. Aminov, R.S. Iskandarov and Kh. T. Avezov*, Chem. Natural Comp.*, 34, 590, 1998.
53. M.F.R. Fouda, A.A. Yousef Elham, S.S. Mohamed and Z.E. Shoeb, *Grass Y. Aceites*, 52, 317, 2001.
54. Fujita S., Moribe S., Kanamori Y., Kubudate M., Takezawa N., *Appl. catal.,* 207A(1-2), 121, 2001.
55. Kurtz M., Bauer N., Buscher C., Wilmer H., Hinrichsen O., Becker R., Rabe S., Merz K., Driess M., Fischer R.A., Muhler M., *Catal. Lett*., 92, 49, 2004.
56. Moharana SC, Prahraj J and Bhatta D*. Indian J Chem,* 31: 1569, 2002.
57. P.G. More and R.B. Bhalvankar*, J. Indian Chem. Soc*., 81, 31, 2004.
58. S.A. Javed, N. Siddiqui and S. Dradu*, Indian J. Heterocycl. Chem.*, 13, 287, 2004.
59. M. Takenaka and M. Watanabe, Jap. Kokai, Tokkyo, (Japan), 02,101,068, pp 7, 1988; *Chem. Abstr.,* 113, 73019, 1990.
60. N. Mathur, P. Adwani and K.G. Ojha, *Die Pharmazie*, 47, 11H, 1992.
61. Malik KJ, Manvi FV, Nanjwade BK and Singh S:*Drug Invention* Today 1: 32-34, 2009.
62. D.K. Singh, S. Singh and M. Shrivastava*, J. Indian Chem. Soc.,* 82, 250, 2005.
63. Bansod, N. H., Chaudhari, G. N., Thihale, M. S. and Patil, S.D., *Sie Pharma Chhemica*, 5(2), 144-148, 2013.
64. Raje N, Naik VR, Reddy AVR*. Journal of Thermal Analysis and Calorimetry;* 112(1), 187-192, 2013.
65. Teka T., Reda A., *International Journal of Technology Enhancements and Emerging Engineering Research*, 2(10), 6-9, 2014**.**
66. S. A. Kim et al, J. *Antimicrob. Chemother*., 2015.
67. Gmurczyk, M. Parabens: A Source of Concern? *ChemMatters*, *33* (2), pp 8–9, 2015.
68. Pickett, M. Underarm yourself with Chemistry. *ChemMatters*, *32* (2), pp 6–8, 2014**.**